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Yukiko Iwata
Date: June 15, 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#4

In re application of	
EIT DRENT and WILLEM W. JAGER	
Serial No. 09/804,891	Group Art Unit: 1623
Filed March 13, 2001	
PROCESS FOR THE CARBONYLATION OF PENTENENITRILE	June 15, 2001

ASSISTANT COMMISSIONER FOR PATENTS
Washington, DC 20231

Sir:

CLAIM TO PRIORITY

Applicants reaffirm the claim for the benefit of filing date of the following foreign patent applications referred to in Applicants' Declaration:

European application Serial No. 00200927.2 filed March 14, 2000 and

European application Serial No. 00200926.4 filed March 14, 2000

Copies of the applications certified by the European Patent Office are enclosed.

Respectfully submitted,

EIT DRENT and WILLEM W. JAGER

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file 3/13/2001

Eur päisches Patentamt | European Patent Office | Office eur péen des brevets

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

00200927.2

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE, 15/03/01
LA HAYE, LE

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Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: 00200927.2
Demande n°:

Anmeldetag:
Date of filing: 14/03/00
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
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NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Process for the carbonylation of pentenenitrile

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: State: Pays:	Tag: Date: Date:	Aktenzeichen: File no. Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
/

Am Anmeldetag benannte Vertragstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR
Etats contractants désignés lors du depôt:

Bemerkungen:
Remarks:
Remarques:

TS 0982 EPC

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PROCESS FOR THE CARBONYLATION OF PENTENENITRILE

The invention relates to a carbonylation process of pentenenitrile to prepare 4-cyanopentanoic acid or its ester in the presence of a catalyst system.

US-A-4950778 describes a process to prepare 4-cyanopentanoic acid by reacting 3-pentenenitrile with water and carbon monoxide in the presence of a cobalt catalyst at a pressure of 136 bar and a temperature of 200 °C. At a conversion of 87.4% the selectivity to the undesired branched C_6 acids was 9.1% and to the undesired valeronitril was 9.6%.

US-A-5434290 describes a process to prepare methyl 5-cyanovalerate by reacting 3-pentenenitrile with methanol and carbon monoxide in the presence of a cobalt catalyst at a pressure of 200 bar and a temperature of 160 °C. At a conversion of 66% the selectivity to the desired methyl 5-cyanovalerate was about 89%.

A disadvantage of the above processes is the high operating pressure, the use of high concentrations of cobalt carbonyl compounds and the low selectivity's at a relatively low conversion.

US-A-5679831 describes the carbonylation of methyl 3-pentenoate to dimethyl adipate by reacting the methyl-3-pentenoate with methanol and carbon monoxide in the presence of a catalyst system consisting of palladium, 1,1'-bis(diisopropylphosphino)ferrocene and p-toluene sulphonic acid at a pressure of 60 bar and a temperature of 130 °C. At 99% conversion a 83% selectivity to dimethyl adipate was obtained. Another experiment performed at 90 °C illustrated a selectivity of 84% to adipate at a 71% conversion of pentenoate. All

experiments were performed starting with pentenoate and with an acid to palladium molar ratio of above 10. Pentenenitrile is mentioned as a possible substrate instead of pentenoate. However if pentenenitrile is used instead of methyl-3-pentenoate using the same ligand and under the conditions of the examples no catalyst activity is observed. Another disadvantage is that because of the high acid concentration the reaction mixture is corrosive and more ligand degradation results due to quartanization of the phosphine compound with the acid and the olefinic compound.

EP-A-495548 describes the carbonylation of propene by reacting propene with methanol and carbon monoxide in the presence of palladium, 1,3-bis(di-tert.butylphosphino)-propane and methylsulphonic acid at a pressure of 30 bar and a temperature of 60 °C. The selectivity to the desired linear methylbutanoate was 86%.

The invention aims to provide a process for the preparation of 5-cyanovaleric acid or its esters in a high yield and at moderate process conditions.

This aim is achieved by the following process. Process to prepare a 5-cyanovaleric acid or its ester by carbonylation of a pentenenitrile, wherein pentenenitrile is reacted with carbon monoxide and water or an alcohol in the presence of a catalyst system, comprising

(a) a metal of Group VIII or a compound thereof and

(b) a bidentate phosphine, arsine and/or stibine ligand, wherein the bidentate ligand has the general formula (I):

$$R^1R^2\text{-}M^1\text{-}R\text{-}M^2\text{-}R^3R^4 \qquad \text{I}$$

wherein M^1 and M^2 are independently P, As or Sb, R is a divalent organic bridging group, which bridging group comprises a chain of 3 to 5 atoms directly connecting the 2 phosphorus atoms, which chain consists of carbon atoms and optionally a nitrogen,

oxygen or sulphur atom or a silano or dialkylsilicon group, which alkyl groups independently comprise from 1 to 4 carbon atoms, and R^1-R^4 represent the same or different optionally substituted tertiary alkyl groups,

(c) an acid having a pKa less than 3, as measured at 18 °C in an aqueous solution.

Applicants have now found that with the process according to the invention a 5-cyanovaleric acid or ester can be obtained in a high yield under process conditions which are much milder with respect to operating pressure than the cited cobalt catalyzed processes. In view of EP-A-495548 it was unexpected that starting from pentenenitrile a higher selectivity to linear products can be obtained than when starting from a more simple molecule like propene as illustrated in said publication. In view of US-A-5679831 it is unexpected that when using a compound, cited as one of the less preferred starting compounds, a higher yield is obtained than those disclosed in said publication for dimethyl adipate.

The process is especially advantageous because it can be performed at a relatively low temperature. A problem often encountered with the use of catalyst systems comprising palladium, phosphines and acids is that the catalyst stability becomes too low for commercial application at elevated temperatures, especially above 120 °C. Because the catalyst has a commercially acceptable activity at temperatures of below 120 °C and especially below 110 °C less catalyst will be consumed by the process.

Among the metals of Group VIII, cobalt, nickel, palladium, rhodium and platinum may be mentioned. Of these, palladium is in particular preferred. As source of Group VIII metal, hereinafter further exemplified as source of palladium, metallic palladium or, preferably, a

palladium compound may be used, in particular a palladium salt. The palladium compound used in the process of the invention may be provided in the form of a palladium complex of the specified ligand according to formula (I). It may also conveniently be generated in situ by adding a source of palladium and sources of the ligand to the reaction. Suitable sources of palladium include Pd(0)(dibenzylaceton)$_2$, palladium carboxylates, such as palladium acetate, propionate, butyrate or benzoate, and palladium salts of mineral acids. Further sources include palladium complexes such as palladium acetylacetonate, tetrakis(triphenylphosphine)palladium and bis(tri-otolylphosphine)palladium acetate. Palladium may be used in a heterogeneous form such as, for example, loaded on an ion exchange resin.

Furthermore palladium salts of alkanoic acids may be used, in particular alkanoic acids with up to 12 carbon atoms, for example acetic acid, propionic acid or trifluoroacetic acid.

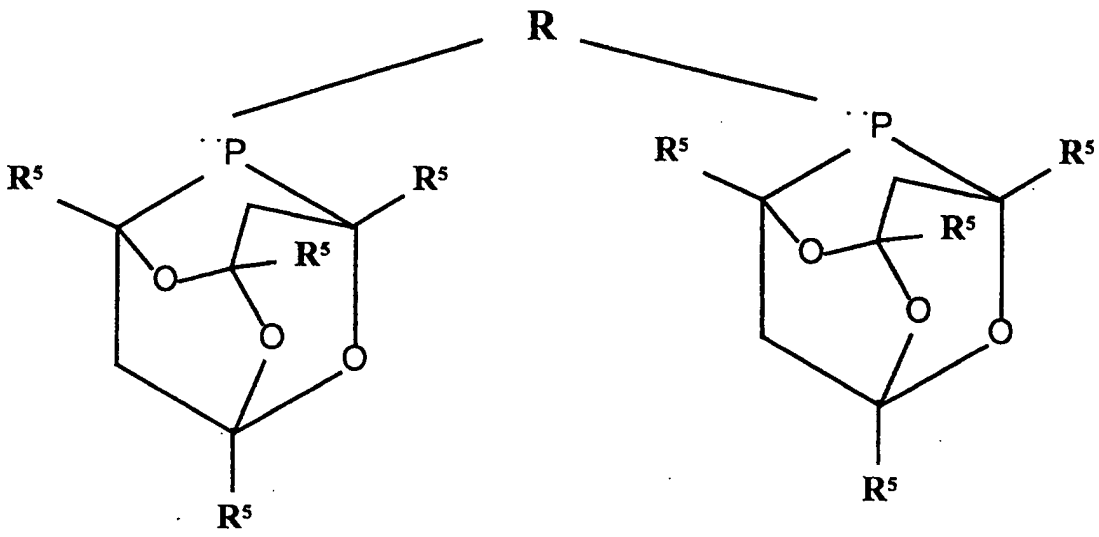
In the bidentate of formula I, M^1 and M^2 are preferably the same and in particular they both represent phosphorus atoms.

For being capable of bidentate coordination to the preferred palladium atom, the bidentate diphosphine ligands of the catalyst system should be free of substituents offering stearic hindrance to a bidentate coordination mode. In particular, the divalent bridging group R should be free of substituents offering stearic hindrance. The bridging group R is preferably an organic divalent group comprising 3 to 20 atoms. Preferably the chain of atoms connecting the two phosphorus atoms does not contain terminal heteroatoms. More preferably the bridging group consists only of carbon atoms. Examples o possible bridging groups are substituted or unsubstitut divalent aryl groups, for example dinaphthyl and dixyly

Another preferred group of bridging groups are C_3-C_5 alkylene groups: trimethylene, tetramethylene and pentamethylene of which trimethylene is most preferred.

The bridging group may optionally be substituted by one or more substituents, provided that the substituents do not offer stearic hindrance to the bidentate ligand coordination mode. Examples of possible substituents are alkyl groups, e.g. of 1 to 4 carbon atoms, alkoxy groups in which the alkyl group comprises from 1 to 3 carbon atoms, dialkylamino groups in which the alkyl groups independently comprise 1 to 3 carbon atoms, or halogen atoms such as bromine and chlorine atoms.

In the present specification the alkyl groups represented by R^1 to R^4 include cyclic structures. R^1 and R^2 and/or R^3 and R^4 may form one cyclic structure, optionally containing heteroatoms. More preferably R^1 and R^2 and/or R^3 and R^4 represents a bivalent radical that together with the phosphorus atom to which it is attached is an alkyl substituted 2-phosphatricyclo[3.3.1.1{3,7}]-decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms. Preferably the ligand comprising the alkyl substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group is a compound according to Formula II, wherein R^5 are alkyl groups of 1-6 carbon atoms, preferably methyl. Examples of such ligands and their preparation are described in more detail in WO-A-9842717.



(II)

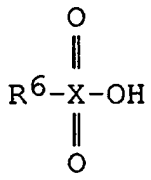
Preferably the tert.alkyl groups are non-cyclic tert. alkyl groups. Examples of suitable non-cyclic tertiary alkyl groups are tertiary butyl, 2-(2-methyl)butyl, 2-(2-ethyl)butyl, 2-(2-methyl)pentyl and 2-(2-ethyl)-pentyl groups. Preferably the groups R^1 to R^4 represent the same secondary or tertiary alkyl groups, most preferably R^1 to R^4 are tert.butyl groups.

Examples of possible ligands are 1,4-bis(di-tertiary-butylphosphino)butane, 1,5-bis(di-tertiarybutyl-phosphino)pentane, 1,3-bis(di-2-(2-methyl)butyl-phosphino)propane, 1,3-bis(di-2-(2-ethyl)butylphosphino)-propane, 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)propane (DPA3), 1,4-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)butane, 1,2-bis(di-2-(2-methyl)butylphosphinomethyl)benzene.

Particularly preferred bidentate ligands are: 1,3-bis(di-tertiarybutylphosphino)propane and 1,2-bis(di-tertiarybutylphosphinomethyl)benzene, wherein the bridging group may be optionally further substituted as described above.

The acid having a pKa below 3.0 preferably has a non-coordinating anion, by which is meant that little or no covalent interaction takes place between the palladium

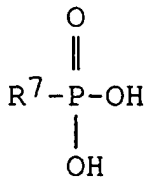
and the anion. Typical examples of such anions are PF_6^-, SbF_6^-, BF_4^- and ClO_4^-. Preferred acids are for example, sulfonic acids and acids that can be formed, possibly in situ, by interacting a Lewis acid such as, for example BF_3, AsF_5, SbF_5, PF_5, TaF_5 or NbF_5 with a Broensted acid such as, for example, a hydrohalogenic acid, in particular HF, fluorosulfonic acid, phosphoric acid or sulfuric acid. Specific examples of acids of the latter type are fluorosilicic acid, HBF_3, HPF_6 and $HSbF_6$. Examples of suitable sulfonic acids are fluorosulfonic acid and chlorosulfonic acid and the hereinafter specified sulfonic acids. A preferred group of acids having a pKa below 3.0 has the general formula III



(III)

wherein X represents a sulphur or a chlorine atom and, if X represents a chlorine atom, R^6 represents an oxygen atom and, if X represents a sulphur atom, R^6 represents an OH group or a hydrocarbon group, for example an alkyl or aryl group, which can either be substituted or unsubstituted. Examples of suitable acids of the general formula III are perchloric acid, sulfuric acid, 2-hydroxypropane-2-sulfonic acid, p-toluenesulfonic acid, tert.butyl sulfonic acid, methyl sulfonic acid. The acid of the general formula III can also be an ion exchanger containing sulfonic acid groups, such as, for example, AMBERLITE 252 H ("AMBERLITE" is a trade name). In that case, the hydrocarbon group R^6 represents a polymeric hydrocarbon group substituted with sulfonic acid groups such as, for example, a polystyrene group.

Another possible acid is according to the following general formula IV



(IV)

wherein R^7 can be an -OH group or a hydrocarbon group, for example an alkyl or aryl group, which can either be substituted or unsubstituted. Examples are phosphoric acid, methyl phosphonic acid, phenyl phosphonic acid.

When the hereinbefore stated acids are used in the process according to the invention, the anions of the acids can be considered to be non-coordinating. The molar ratio of acid and palladium is preferably between 1:1 and 10:1 and more preferably between 1:1 and 5:1.

Since halide ions can be corrosive, the source of palladium in the catalyst systems of the invention is preferably not a halide or a compound generating halide ions. Small amounts of halide however may be advantageously present. Optionally other promoters may be present.

Conveniently the catalyst system of the invention is obtained by combining in a separate step, preceding the carbonylation reaction, the source of palladium and the bidentate ligand of formula I. Suitably the palladium compound, as exemplified hereinbefore, is dissolved in a suitable solvent, and subsequently admixed with the bidentate. The molar ratio between the bidentate ligand and the palladium source (a) is preferably in the range of 1:1 to 5:1 and, more preferably, in the range of 1:1 to 3:1. The possibility of applying these low molar ratios is advantageous, as it avoids the use of an excess

of bidentate ligand and hence minimises the consumption of these usually expensive compounds.

The amount of catalyst used in the process is not critical. Good results are obtained when the amount of Group VIII metal is in the range of 10^{-7} to 10^{-1} gram atom per mole of pentenenitrile. Preferably this amount is in the range of 10^{-5} to 5.10^{-2} gat per mole.

If the carbonylation process is carried out in the presence of water, the product obtained will be 5-cyanovaleric acid. By-products will be mainly small amounts of branched cyano acids. 5-cyanovaleric acid is preferably obtained by hydrolysis of the 5-cyanovalerate ester as obtained by the process according to the invention.

In the process according to the invention, 5-cyanovaleric esters may be obtained directly, if the carbonylation is carried out in the presence of an alcohol. Suitable alcohols include aliphatic mono alcohols, in particular those having from 1-6 carbon atoms per molecule such as methanol, ethanol, propanol, butanol, isopropanol, phenol and dihydric alcohols such as ethylene glycol and 1,3-propane diol. Methanol is in particular preferred. When a 5-cyanovalerate ester is the desired product, the presence of water is preferably avoided. More preferably the process is performed in the presence of a water scavenger, for example trimethyl ortho formate.

The amount of alcohol or water is not critical. The mol ratio water or alcohol to pentenitrile may range from about equimolar to an excess of water or alcohol. Optionally the alcohol or water may serve as reaction solvent as well, although, if desired, separate solvents may also be used.

Additional solvents, if present, are preferably compounds which weakly co-ordinate with the palladium

compound. Examples of suitable solvents are acetonitrile, ethanol, acetone, acetylacetone, toluene, sulfolane, and ethers, for example dimethyl ether of diethylene glycol, anisole diphenyl ether.

The carbonylation reaction according to the invention is carried out at moderate temperatures and pressures. Suitable reaction temperatures are in the range of 50-250 °C, preferably in the range of 80-120 °C. The reaction pressure is usually at least atmospheric. Suitable pressures are in the range of 1 to 100 bar, preferably in the range of 5 to 50 bar.

The carbon monoxide required for the reaction may be supplied in substantially pure form, or contaminated with in general minor amounts of inert compounds such as nitrogen, hydrogen and the like.

The process may be carried out in batch operation or continuously. In embodiments relating to continuous operation of the process, products are conveniently isolated from the catalyst system by means of distillation, preferably in a wiped film evaporator. Alternatively the products can be stripped from the reaction mixture with the aid of a gas.

The starting pentenenitrile may be a 2-, 3- or 4-pentenenitrile or their mixtures. It has been found that from all these starting compounds a high selectivity to linear products is obtained with the process according to the invention. Pentenenitrile may be advantageously be obtained by a process as described in for example US-A-4,298,546 and US-A-5,821,378 starting from butadiene and hydrogen cyanide.

The 5-cyanovaleric acid or ester can be used as an intermediate to prepare adipic acid or its ester and ε-caprolactam. Adipic acid can be obtained by esterfication of the cyano group. Adipic acid is a precursor to Nylon-6.6 The other precursor to Nylon-6.6

is 1,3 di-cyanopropane which is typically prepared from pentenenitrile. The present process therefore provides a manufacturer of Nylon-6.6 or its precursors an favourable route to adipic acid from a precursor which is already used to prepare 1,3 di-cyanopropane.

ε-Caprolactam can be advantageously be obtained by reduction of the cyano-group to an amine by making use of generally known reduction techniques and subsequently cyclisizing the obtained 6-aminocaproic acid or ester at elevated temperatures.

Reducing the cyano group to a amine group can be performed by well known reducing techniques, wherein hydrogen is contacted with the cyano compound in the presence of a reducing catalyst, suitably Cu or a Group VIII metal as for example Pt, Pd, Ni, Co, Ru, or Fe. This catalyst can be a homogeneous catalyst, for example the catalyst used in the carbonylation process according to the invention. Preferably a heterogeneous catalyst is used. Examples of reducing catalysts are Raney Ni, Raney Cobalt, and Co/Cu catalysts.

Cyclisizing of the obtained 6-aminocaproic acid or ester is suitably performed in a suitable solvent at an elevated temperature. See for example US-A-4731445. Suitable solvents are water, high boiling hydrocarbons and alcohols, preferably the corresponding alcohol of the 6-aminocaproate ester. Preferably water is used as the solvent and 6-aminocaproic acid is used as the compound in step (c) as for example described in US-A-5780623. The temperature is preferably between 280 and 350 °C. If a 5-cyanovalerate ester is obtained by the process according to the invention it may be advantageous to first hydrolyse this compound to its corresponding acid prior to either the reduction or the cyclisation. Alternatively 6-aminocaproic acid and/or its ester may be directly reacted to ε-caprolactam in the presence of

super heated steam at a temperature of between 270 and 350 °C and a pressure of between 5 and 20 bar as exemplified in WO-A-9837063.

It can be advantageous according to US-A-5,780,623 to perform the cyclisation step starting from the 6-aminocaproic acid in an aqueous solution and in the absence of an alcohol. When a 5-cyanovalerate ester is obtained by the process according to the invention it may therefore be advantageous to first hydrolyse this compound to its corresponding acid prior to either the reduction step or the cyclisation step. More preferably 5-cyanovaleric acid as obtained by the process according the invention is used to prepare ε-caprolactam. This eliminates the use and re-use of an alcohol and the associated hydrolysis step. A problem associated with the preparation of 5-cyanovaleric acid is however that it is difficult to separate this product from the branched cyano acids which are formed as by-product by means of distillation. A possible advantageous option could be to perform the reduction step and cyclization starting from the mixture of both branched and linear cyano-acids. The desired ε-caprolactam can subsequently be isolated in a more simple manner from the then formed lactam by-products by for example crystallization or distillation.

The invention is also directed to a process to prepare ε-caprolactam starting from pentenenitrile by (a) first performing the carbonylation process as described above, (b) isolating the 5-cyanovaleric acid or ester from the catalyst system (c) reduction of the cyano group in which 6-aminocaproic acid or ester is obtained and (d) cyclisizing 6-aminocaproic acid or ester to ε-caprolactam. Optionally the branched and linear cyano acid or ester products as obtained in the carbonylation step are isolated prior to step (c) or step (d). As

explained above it can be advantageous to leave out this separation and perform this separation together with the purification of the ε-caprolactam.

The invention may be illustrated by the following non-limiting examples.

Examples 1-13

Examples 1-13 were carried out in a magnetically stirred 250 ml Autoclave (Hastelloy C, trade mark). The autoclave was charged with methanol, and an optional solvent, in the amounts given and 20 ml of 3-pentenenitrile, 0.25 mmol palladium(II) acetate, the selected phosphine and the acid in the amounts given. The Palladium acetate/phosphine were charged under a nitrogen atmosphere. After closure of the autoclave it was evacuated, whereupon 60 bar of CO was supplied. The autoclave was heated to the desired temperature. The initial rate of carbonylation was determined from the pressure decrease per time unit during the first hour of reaction. After a total reaction time of 10 hours the autoclave was cooled to room temperature and slowly depressurized thereafter. The selectivities, linearity of cyano-ester products and conversion were determined by gas liquid chromatographic analysis of the reaction products. See Table 1 for solvents, amounts, conditions and results.

Example 14

Example 1 was repeated except that 0.6 mmol of 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)propane (DPA3) was used as the ligand in the presence of 0.5 ml CH_3SO_3H, 10 ml pentenenitrile and 40 ml methanol at 115 °C. The initial rate (mol/mol/hr) was 100. The conversion was 70% after 10 hours. The selectivity to cyano-esters was 98%. The linearity was 88%.

Ex.	ligand (mmol)	acid (mmol)	reaction medium (ml)	temp. (°C)	initial rate (mol/ mol/hr)	conver-sion (%)	selectivi-ty to cyano-esters (mol%)	linearity (mol%) (1)
1	1,3 bis(di-tert-butylphosphino)-propane (0.6)	CH_3SO_3H(2)	CH_3OH(40)	115	200	85	98	93
2	1,3 bis(di-iso-propylphoshino)-propane (0.6)	ditto (2)	ditto(40)	115	trace	<2	-	-
3	1,3 bis(di-tert-butylphosphino)-propane (0.6)	ditto (2)	ditto(40)	100	300	94	98	93
4	1,3 bis(di-tert-butylphosphino)-propane (0.6)	ditto (1)	ditto(40)	100	350	84	98	93
5	1,3 bis(di-tert-butylphosphino)-propane (0.6)	t-$BuSO_3H$(2)	ditto(40)	100	350	95	98	94

Ex.	ligand (mmol)	acid (mmol)	reaction medium (ml)	temp. (°C)	initial rate (mol/ mol/hr)	conver-sion (%)	selectivi-ty to cyano-esters (mol%)	linearity (mol%) (1)
6	1,3 bis(di-tert-butylphosphino)-propane (0.6)	ditto (2)	ditto(40)	90	250	87	98	94
7	1,3 bis(di-tert-butylphosphino)-propane (0.6)	ditto (2)	ditto(40)	125	400	96	98	93
8	1,2 bis(di-tert-butylphosphino)-ethane (0.6)	ditto (2)	ditto(40)	100	<10	5	95	88
9	1,3 bis(di-tert-butylphosphino)-propane (0.6)	ditto (2)	CH_3OH(10), anisole (30)	100	400	96	98	96
10	1,3 bis(di-cyclo-hexylphosphino)-propane (0.6)	ditto (2)	CH_3OH(10), anisole (30)	100	trace	<2	-	-

Ex.	ligand (mmol)	acid (mmol)	reaction medium (ml)	temp. (°C)	initial rate (mol/ mol/hr)	conver-sion (%)	selectivi-ty to cyano-esters (mol%)	linearity (mol%) (1)
11	1,1' bis (di-isopropylphos-phino) ferrocene (0.6)	ditto (2)	CH_3OH(10), anisole (30)	100	trace	<2	-	-
12	1,2-bis(di-tert-butylphosphino-methyl)benzene (0.6)	CH_3SO_3H (1)	CH_3OH(10), anisole (30)	100	150	60	98	98
13	tri-tertbutyl phoshine (mono-phosphine) (0.6)	ditto (1)	CH_3OH(10), anisole (30)	100	trace	<1	-	-

(1) linearity is the mol percentage of 5-cynaovalerate ester relative to all cyano-esters.

Note: Pentenentrile composition at intermediate conversions show a mixture of cis + trans -2-pentenenitriles, and cis + trans 3-pentenenitriles showing that all isomers can be converted to 4 cyano-methyl pentanoate.

C L A I M S

1. Process to prepare a 5-cyanovaleric acid or its ester by carbonylation of a pentenenitrile, wherein pentenenitrile is reacted with carbon monoxide and water or an alcohol in the presence of a catalyst system, comprising

(a) a metal of Group VIII or a compound thereof and

(b) a bidentate phosphine, arsine and/or stibine ligand, wherein the bidentate ligand has the general formula (I):

$$R^1R^2\text{-}M^1\text{-}R\text{-}M^2\text{-}R^3R^4 \qquad I$$

wherein M^1 and M^2 are independently P, As or Sb, R is a divalent organic bridging group, which bridging group comprises a chain of 3 to 5 atoms directly connecting the 2 phosphorus atoms, which chain consists of carbon atoms and optionally a nitrogen, oxygen or sulphur atom or a silano or dialkylsilicon group, which alkyl groups independently comprise from 1 to 4 carbon atoms, and R^1-R^4 represent the same or different optionally substituted tertiary alkyl groups,

(c) an acid having a pKa less than 3, as measured at 18 °C in an aqueous solution.

2. A process as claimed in claim 1, wherein the bidentate ligand of formula I is a bisphosphine ligand and R^1-R^4 represent the same tertiary alkyl groups.

3. A process as claimed in claim 1 or 2, wherein R^1-R^4 represent tertiary butyl groups.

4. Process according to any one of claims 1-3, wherein R is a C_3-C_5 alkylene group.

5. A process as claimed in claim 4, wherein the bidentate ligand is 1,3-bis(di-tert.butylphosphino)-propane or 1,2-bis(di-tert.butylphosphinomethyl)benzene.

6. A process as claimed in one or more of claims 1-5, wherein the Group VIII metal is palladium.

7. A process as claimed in one or more of claims 1-6, wherein the molar ratio between the ligand and the metal (a) is in the range of 1:1 to 5:1.

8. Process according to any one of claims 1-7, wherein the temperature is between 80 and 120 °C.

9. Process according to any one of claims 1-7, wherein the molar ratio of acid compound (c) and metal compound (a) is between 1:1 and 5:1.

10. Process according to any one of claims 1-9, wherein 5-cyanovaleric acid is obtained.

11. Process according to any one of claims 1-9, wherein methyl 5-cyanovalerate is obtained.

12. Process to prepare ε-caprolactam starting from pentenenitrile by (a) first performing the process according to any one of claims 1-11, (b) isolating the 5-cyanovaleric acid or ester from the catalyst system, (c) reduction of the cyano group in which 6-aminocaproic acid or ester is obtained and (d) cyclisizing 6-aminocaproic acid or ester to ε-caprolactam.

13. Process according to claim 12, wherein both branched and linear products obtained in step (a) are subjected to steps (b), (c) and (d).

filed 3/13/2001

Europäisches Patentamt	European Patent Office	Office européen des brevets

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.	The attached documents are exact copies of the European patent application described on the following page, as originally filed.	Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

00200926.4

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

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Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: 00200926.4
Demande n°:

Anmeldetag:
Date of filing: 14/03/00
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
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NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Process for the preparation of epsilon-caprolactam

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: State: Pays:	Tag: Date: Date:	Aktenzeichen: File no. Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
/

Am Anmeldetag benannte Vertragstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR
Etats contractants désignés lors du depôt:

Bemerkungen:
Remarks:
Remarques:

PROCESS FOR THE PREPARATION OF ε-CAPROLACTAM

The invention relates to a new route to ε-caprolactam starting from butadiene or a butadiene derivative.

In the field of preparing ε-caprolactam there is a great need for a new route based on butadiene. Commercial processes for the preparation of ε-caprolactam use either phenol or cyclohexane as starting compounds. A disadvantage of these routes is that ammonium sulphate is produced as an unwanted by-product. Furthermore these known processes include numerous process steps, which makes the preparation of ε-caprolactam a laborious and costly process.

In recent patent literature a butadiene based preparation of ε-caprolactam is described wherein first a pentenoate ester is prepared by carbonylation of butadiene, which in turn is reacted to 5-formylvalerate ester in a hydroformylation step. The 5-formylvalerate ester is subsequently converted to 6-aminocaproic acid or its ester in a reductive amination step. 6-aminocaproic acid or its ester is subsequently reacted to ε-caprolactam upon heating in an aqueous medium. According to US-A-5693851, which describes a palladium catalysed carbonylation of butadiene at 140 °C , the best selectivity to methyl 3- and 4-pentenoate ester is about 93%. According to US-A-6018081, which describes a rhodium catalysed hydroformylation of methyl pentenoate ester, the best selectivity to methyl 5-formylvalerate ester is 81%. According to EP-A-729943 and WO-A-9837063 a 100% conversion of methyl 5-formylvalerate to ε-caprolactam is achievable in the reductive amination and cyclisation

steps. Based on butadiene the overall selectivity is thus at most about 75%. This means that 25% of the starting butadiene is converted to by-products which have to be disposed off. It will be evidently clear that this overall selectivity will have to be significantly improved before a commercial application can be conceived.

The object of the present invention is to provide a route to ε-caprolactam with a higher overall selectivity based on butadiene or a butadiene derivative. This object is achieved by the following process:

Process to prepare ε-caprolactam from pentenenitrile, wherein the following steps are performed:

(a) carbonylation of pentenenitrile to 5-cyanovaleric acid or ester by reacting pentenenitrile with carbon monoxide and water or an alcohol in the presence of a catalyst system, comprising palladium, a bidentate phosphine ligand and an acid having a pKa less than 3, as measured at 18 °C in an aqueous solution,

(b) reduction of 5-cyanovaleric acid or ester as obtained in step (a) to 6-aminocaproic acid or ester,

(c) cyclisation of the 6-aminocaproic acid or ester to ε-caprolactam.

Applicants have found that with the process according to the invention ε-caprolactam can be obtained with a high selectivity based on pentenenitrile, which in turn can be prepared from butadiene in a high selectivity, >95% according to US-A-5821378. Applicants have now found that step (a) of the present process can be performed with a 94% selectivity to 5-cyanovalerate ester at 96% conversion of pentenenitrile. Because step (b) and (c) of the process according to the invention are, with respect to their chemistry, very comparable with the reductive amination and cyclisations steps as exemplified in the

above references a comparable selectivity of about 100% may be assumed. Thus by using pentenenitrile, as obtained at a 95% selectivity from butadiene, in the present process an overall selectivity of about 90% or more, based on butadiene, to ε-caprolactam is possible. Pentenenitrile is moreover an advantageous intermediate because it can be prepared from butadiene by means of commercially proven technology. As such the carbonylation of pentenenitrile is known and described in various publications. However up till now a commercially interesting technology has not been developed. With the present process, incorporating a very selective carbonylation step (a), which can be performed at acceptable pressure ranges and catalyst usage, a favourable alternative route to ε-caprolactam is obtained.

Step (a) can be performed at a relatively low temperature. This is advantageous because a problem often encountered with the use of catalyst systems comprising palladium, phosphines and acids, as for example described in above cited US-A-5693851, is that the catalyst stability becomes too low for commercial application at elevated temperatures, especially above 120 °C. Because the carbonylation reaction of the process according to the present invention has a commercially acceptable activity at temperatures of below 120 °C and especially below 110 °C, less catalyst will be consumed by the process.

As source of palladium metallic palladium or, preferably, a palladium compound may be used, in particular a palladium salt. The palladium compound used in the process of the invention may be provided in the form of a palladium complex of the specified bidentate phosphine ligand. It may also conveniently be generated

in situ by adding a source of palladium and sources of the ligand to the reaction. Suitable sources of palladium include Pd(0)(dibenzylaceton)$_2$ and palladium carboxylates, such as palladium acetate, propionate, butyrate or benzoate, and palladium salts of mineral acids. Further sources include palladium complexes such as palladium acetylacetonate, tetrakis(triphenylphosphine)palladium and bis(tri-otolylphosphine)palladium acetate. Palladium may be used in a heterogeneous form such as, for example, loaded on an ion exchange resin. Furthermore palladium salts of alkanoic acids may be used, in particular alkanoic acids with up to 12 carbon atoms, for example acetic acid, propionic acid or trifluoroacetic acid.

The bidentate ligand used in step (a) is preferably a compound according to general formula (I):

$$R^1R^2\text{-}P\text{-}R\text{-}P\text{-}R^3R^4 \qquad I$$

wherein R comprises an optionally substituted chain of three or more atoms which directly connect the two phosphorus atoms and R^1-R^4 represent the same or different optionally substituted hydrocarbon group.

For being capable of bidentate co-ordination to the preferred palladium atom, the bidentate phosphine ligands of the catalyst system should be free of substituents offering stearic hindrance to a bidentate co-ordination mode. In particular, the divalent bridging group R should be free of substituents offering stearic hindrance. The bridging group R is preferably an organic divalent group comprising 3 to 20 atoms. Preferably the chain of atoms connecting the two phosphorus atoms does not contain terminal heteroatoms. More preferably the bridging group consists only of carbon atoms. Examples of possible bridging groups are substituted or unsubstituted divalent aryl groups, for example dinaphthyl and di-xylyl. Most

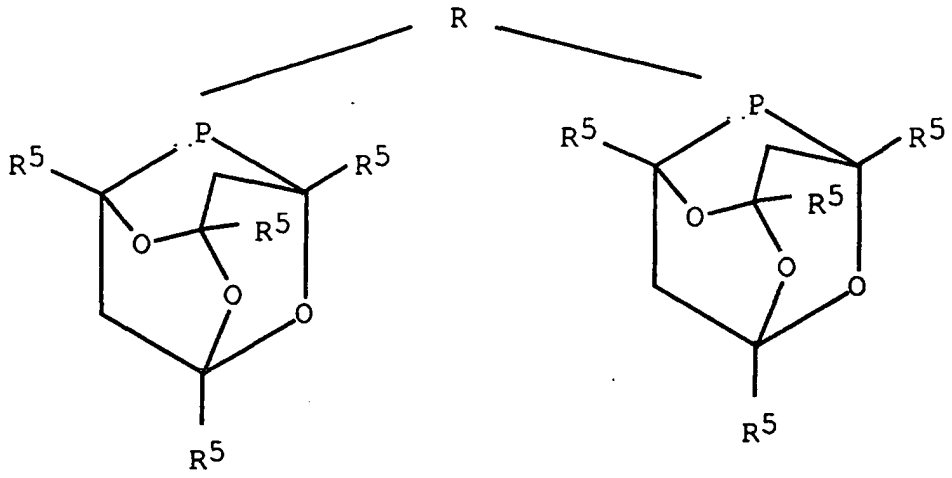
preferred bridging groups are C_3-C_5 alkylene groups: trimethylene, tetramethylene and pentamethylene of which trimethylene is most preferred.

The bridging group R may optionally be substituted by one or more substituents, provided that the substituents do not offer stearic hindrance to the bidentate ligand co-ordination mode. Examples of possible substituents are alkyl groups, e.g. of 1 to 4 carbon atoms, alkoxy groups in which the alkyl group comprises from 1 to 3 carbon atoms, dialkylamino groups in which the alkyl groups independently comprise 1 to 3 carbon atoms, or halogen atoms such as bromine and chlorine atoms.

R^1 to R^4 may suitably be hydrocarbon groups comprising between 2 and 20 carbon atoms. Examples are alkyl groups, for example isopropyl, isobutyl, isopentyl and cyclohexyl and aryl groups, for example phenyl and naphthyl. R^1 and R^2 and/or R^3 and R^4 may form one divalent hydrocarbon group.

Preferably R^1 to R^4 are tertiary alkyl groups. In the present specification the tertiary alkyl groups include cyclic structures. Additionally R^1 and R^2 and/or R^3 and R^4 may form one cyclic structure, optionally containing heteroatoms. More preferably R^1 and R^2 and/or R^3 and R^4 represents a bivalent radical that together with the phosphorus atom to which it is attached is an alkyl substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms. Preferably the ligand comprising the alkyl substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group is a compound according to Formula II, wherein R^5 are alkyl groups of 1-6 acrbon atoms, preferably methyl. Examples of such

ligands and their preparation are described in more detail in WO-A-9842717.



(II)

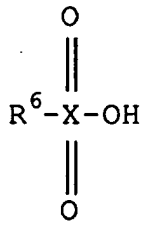
Preferably the tert. alkyl groups are non-cyclic tert. alkyl groups. Examples of suitable non-cyclic tertiary alkyl groups are tertiary butyl, 2-(2-methyl)butyl, 2-(2-ethyl)butyl, 2-(2-methyl)pentyl and 2-(2-ethyl)pentyl groups. Preferably the groups R^1 to R^4 represent the same secondary or tertiary alkyl groups, most preferably R^1 to R^4 are tert. butyl groups.

Examples of possible ligands are
1,4-bis(di-tertiarybutylphosphino)butane,
1,5-bis(di-tertiarybutylphosphino)pentane,
1,3-bis(di-2-(2-methyl)butylphosphino)propane,
1,3-bis(di-2-(2-ethyl)butylphosphino)propane,
1,1'-bis(di-tertiarybutylphosphino)ferrocene,
1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)propane (DPA3),
1,4-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)butane,
1,2-bis(di-2-(2-methyl)butylphosphinomethyl)benzene

Particularly preferred bidentate ligands are:
1,3-bis(di-tertiarybutylphosphino)propane and

1,2-bis(di-tertiary-butylphosphinomethyl)benzene, wherein the bridging group may be optionally further substituted as described above.

The acid having a pKa below 3.0 preferably has a non co-ordinating anion, by which is meant that little or no covalent interaction takes place between the palladium and the anion. Typical examples of such anions are PF_6^-, SbF_6^-, BF_4^- and ClO_4^-. Preferred acids are for example, sulfonic acids and acids that can be formed, possibly in situ, by interacting a Lewis acid such as, for example BF_3, AsF_5, SbF_5, PF_5, TaF_5 or NbF_5 with a Broensted acid such as, for example, a hydrohalogenic acid, in particular HF, fluorosulfonic acid, phosphoric acid or sulfuric acid. Specific examples of acids of the latter type are fluorosilicic acid, HBF_3, HPF_6 and $HSbF_6$. Examples of suitable sulfonic acids are fluorosulfonic acid and chlorosulfonic acid and the hereinafter specified sulfonic acids. A preferred group of acids having a pKa below 3.0 has the general formula III:

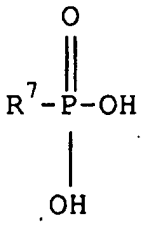


(III)

wherein X represents a sulfur or a chlorine atom and, if X represents a chlorine atom, R^6 represents an oxygen atom and, if X represents a sulfur atom, R^6 represents an -OH group or a hydrocarbon group, for example an alkyl or aryl group, which can either be substituted or unsubstituted. Examples of suitable acids of the general formula III are perchloric acid, sulfuric acid, 2-hydroxypropane-2-sulfonic acid, p-toluenesulfonic acid, tert. butyl sulfonic acid, methyl sulfonic acid. The acid of the general formula III can also be an ion exchanger

containing sulfonic acid groups, such as, for example, Amberlite 252 H ("Amberlite" is a trade name). In that case, the hydrocarbon group R^6 represents a polymeric hydrocarbon group substituted with sulfonic acid groups such as, for example, a polystyrene group.

Another possible acid is according to the following general formula IV:



(IV)

wherein R^7 can be an -OH group or a hydrocarbon group, for example an alkyl or aryl group, which can either be substituted or unsubstituted. Examples are phosphoric acid, methyl phosphonic acid, phenyl phosphonic acid.

When the hereinbefore stated acids are used in the process according to the invention, the anions of the acids can be considered to be non-coordinating. The molar ratio of acid and palladium is preferably between 1:1 and 10:1 and more preferably between 1:1 and 5:1.

Since halide ions can be corrosive, the source of palladium in the catalyst systems of the invention is preferably not a halide or a compound generating halide ions. Small amounts of halide however may be advantageously present. Optionally other promoters may be present.

Conveniently the catalyst system of the invention is obtained by combining in a separate step, preceding the carbonylation reaction, the source of palladium and the bidentate ligand of formula I. Suitably the palladium compound, as exemplified hereinbefore, is dissolved in a suitable solvent, and subsequently admixed with the bidentate. The molar ratio between the bidentate ligand

and palladium is preferably in the range of 1:1 to 5:1 and, more preferably, in the range of 1:1 to 3:1. The possibility of applying these low molar ratios is advantageous, as it avoids the use of an excess of bidentate ligand and hence minimizes the consumption of these usually expensive compounds.

The amount of catalyst used in the process is not critical. Good results are obtained when the amount of palladium is in the range of 10^{-7} to 10^{-1} gram atom per mole of pentnenitrile. Preferably this amount is in the range of 10^{-5} to 5.10^{-2} gat per mole.

If the carbonylation process is carried out in the presence of water, the product obtained will be 5-cyanovaleric acid. By-products will be mainly small amounts of branched cyano acids. If 5-cyanovaleric acid is the desired intermediate product after step (a), it is preferably obtained by first preparing the 5-cyanovalerate ester as described below and subsequently performing a hydrolysis step.

In the process according to the invention, 5-cyanovaleric esters may be obtained if the carbonylation is carried out in the presence of an alcohol. Suitable alcohols include aliphatic mono alcohols, in particular those having from 1-6 carbon atoms per molecule such as methanol, ethanol, propanol, butanol, isopropanol, phenol and dihydric alcohols such as ethylene glycol and 1,3-propane diol. Methanol is in particular preferred. When a 5-cyanovalerate ester is the desired product, the presence of water is preferably avoided. More preferably the process is performed in the presence of a water scavenger, for example trimethyl ortho formate.

The amount of alcohol or water is not critical. The mol ratio water or alcohol to pentenenitrile may range

from about equimolar to an excess of water or alcohol. Optionally the alcohol or water may serve as reaction solvent as well, although, if desired, separate solvents may also be used.

Additional solvents, if present, are preferably compounds which weakly co-ordinate with the palladium compound. Examples of suitable solvents are acetonitrile, ethanol, acetone, acetylacetone, toluene, sulfolane, and ethers, for example dimethyl ether of diethylene glycol, anisole and diphenyl ether. Preferably a solvent is used which has a higher boiling point than the products and by-products obtained in the carbonylation reaction. This enables a simple separation of the homogeneous catalyst system, remaining in the solvent, and the (by-)products by means of distillation. Examples of such solvents are sulfolane and diphenyl ether. Alternative solvents are those in which the homogeneous catalyst is miscible and at the same time does not mix with the carbonylation products. This enables a separation of the homogeneous catalyst system and the products by means of phase separation.

The carbonylation reaction according to the invention is carried out at moderate temperatures and pressures. Possible reaction temperatures are in the range of 50-250 °C, preferably in the range of 80-120 °C. As explained above temperatures of below 130 °C are advantageous because less catalyst consumption will take place. The reaction pressure is usually at least atmospheric. Suitable pressures are in the range of 1 to 100 bar, preferably in the range of 5 to 50 bar.

The carbon monoxide required for the reaction may be supplied in substantially pure form, or contaminated with in general minor amounts of inert compounds such as nitrogen, hydrogen and the like.

The starting pentenenitrile may be a 2-, 3- or 4-pentenenitrile or their mixtures. It has been found that from all these starting compounds a high selectivity to linear products is obtained with the process according to the invention. Pentenenitrile may be advantageously be obtained by a process as described in for example US-A-4298546 and US-A-5821378 starting from butadiene and hydrogen cyanide.

The 5-cyanovaleric acid or ester as obtained in step (a) can be separated from the homogeneous catalyst system by for example distillation, extraction, phase separation or crystallisation, of which distillation is preferred. The catalyst system is advantageously re-used in the carbonylation reaction.

Even though a high selectivity is achieved in step (a) some by-products are formed. These by-products can for example be separated from the 5-cyanovaleric acid or ester by means of distillation or by one of the above mentioned techniques. It can be advantageous to process a mixture of carbonylation products obtained in step (a) in steps (b) and optionally also in step (c). This reduces the amount of purification steps after step (a). Because after step (c) a rigorous purification of ε-caprolactam will always take place it is advantageous to combine these purification steps with the separation of the by-products of the carbonylation. This is especially possible with the present process because the content of by-products is low when compared to the state of the art routes to ε-caprolactam. This is especially advantageous when 5-cyanovaleric acid is the product obtained in step (a). In view of their close boiling points it is not simple to separate the branched compounds from the desired 5-cyanovaleric acid. By not separating these acids in step (a), but instead further processing them as

a mixture in steps (b) and (c) a more simple process is obtained. Separating the ε-caprolactam from the resulting branched lactams after step (c) can be simply performed by for example crystallization or distillation.

Optionally the homogeneous catalyst used in step (a) is separated from the reaction mixture after step (b).

Step (b) can be performed by well known reducing techniques. In this step hydrogen is contacted with the cyano compound obtained in step (a) in the presence of a reducing catalyst, suitably Cu or a Group VIII metal as for example Pt, Pd, Ni, Co, Ru, or Fe. This catalyst can be a homogeneous catalyst, for example the catalyst used in step (a). Preferably a heterogeneous catalyst is used. Examples of reducing catalysts are Raney Ni, Raney Cobalt, and Co/Cu catalysts.

Step (c) is suitably performed in a suitable solvent at an elevated temperature. Suitable solvents are water, high boiling hydrocarbons and alcohols, preferably the corresponding alcohol of the 6-aminocaproate ester. Preferably water is used as the solvent and 6-aminocaproic acid is used as the starting compound in step (c) as for example described in US-A-5780623. The temperature is preferably between 280 and 400 °C. If a 5-cyanovalerate ester is obtained in step (a) it may therefore be advantageous to first hydrolyse this compound to its corresponding acid prior to the reduction step (b) or the cyclisation step (c). Alternatively the hydrogenated product of step (b), i.e. 6-aminocaproic acid or its ester may be reacted to ε-caprolactam in the presence of super heated steam at a temperature of between 270 and 350 °C and a pressure of between 5 and 20 bar as exemplified in WO-A-9837063.

Step (a) is illustrated by the following non-limiting Examples.

Examples 1-11

Examples 1-11 were carried out in a magnetically stirred 250 ml Autoclave (HASTELLOY C, trade mark). The autoclave was charged with methanol, and an optional solvent, in the amounts given and 20 ml of 3-pentenenitrile, 0.25 mmol palladium(II) acetate, the selected phosphine and the acid in the amounts given. The Palladium acetate/phosphine were charged under a nitrogen atmosphere. After closure of the autoclave it was evacuated, whereupon 60 bar of CO was supplied. The autoclave was heated to the desired temperature. The initial rate of carbonylation was determined from the pressure decrease per time unit during the first hour of reaction. After a total reaction time of 10 hours the autoclave was cooled to room temperature and slowly depressurized thereafter. The selectivities, linearity of cyano-ester products and conversion were determined by gas liquid chromatographic analysis of the reaction products. See Table 1 for amounts, solvents, conditions and results.

Example 12

Example 1 was repeated except that 0.6 mmol of 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-tri-oxatricyclo[3.3.1.1{3.7}decyl)propane (DPA3) was used as the ligand in the presence of 0.5 ml CH_3SO_3H, 10 ml pentenenitrile and 40 ml methanol at 115 °C. The initial rate (mol/mol/hr) was 100. The conversion was 70% after 10 hours. The selectivity to cyano-esters was 98%. The linearity was 88%.

Example	ligand (mmol)	acid (mmol)	reaction medium (ml)	temperature (°C)	initial rate (mol/mol/hr)	conversion (%)	selectivity to cyano-esters (mol%)	linearity (mol%) (1)
1	1,3 bis(di-tert-butylphosphino)propane (0.6)	CH_3SO_3H (2)	CH_3OH (40)	115	200	85	98	93
2	1,3 bis(di-isopropyl-phoshino)propane (0.6)	ditto (2)	ditto (40)	115	trace	<2	-	-
3	1,3 bis(di-tert-butyl-phosphino)propane (0.6)	ditto (2)	ditto (40)	100	300	94	98	93
4	1,3 bis(di-tert-butyl-phosphino)propane (0.6)	ditto (1)	ditto (40)	100	350	84	98	93

Example	ligand (mmol)	acid (mmol)	reaction medium (ml)	tempe-rature (°C)	initial rate (mol/mol /hr)	con-version (%)	selec-tivity to cyano-esters (mol%)	linea-rity (mol%) (1)
5	1,3 bis(di-tert-butylphos-phino)propane (0.6)	t-$BuSO_3H$ (2)	ditto (40)	100	350	95	98	94
6	1,3 bis(di-tert-butylphos-phino)propane (0.6)	ditto (2)	ditto (40)	90	250	87	98	94
7	1,3 bis(di-tert-butylphos-phino)propane (0.6)	ditto (2)	ditto (40)	125	400	96	98	93
8	1,2 bis(di-tert-butylphos-phino)ethane (0.6)	ditto (2)	ditto (40)	100	<10	5	95	88
9	1,3 bis(di-tert-butylphos-phino)propane (0.6)	ditto (2)	CH_3OH (10), anisole (30)	100	400	96	98	96

Example	ligand (mmol)	acid (mmol)	reaction medium (ml)	tempe-rature (°C)	initial rate (mol/mol /hr)	con-version (%)	selec-tivity to cyano-esters (mol%)	linea-rity (mol%) (1)
10	1,2-bis(di-tert-butylphos-phinomethyl)benzene (0.6)	CH_3SO_3H (1)	CH_3OH (10), anisole (30)	100	150	60	98	98
11	tri-tertbutyl phoshine (monophosphine) (0.6)	ditto (1)	CH_3OH (10), anisole (30)	100	trace	<1	-	-

(1) linearity is the mol percentage of 5-cyanovalerate ester relative to all cyano-esters

Note: Pentenentrile composition at intermediate conversions show a mixture of cis +trans -2-pentenenitriles, and cis +trans -3-pentenenitriles showing that all isomers can be converted to 4 cyano-methyl pentanoate.

C L A I M S

1. Process to prepare ε-caprolactam from pentenenitrile, wherein the following steps are performed:
(a) carbonylation of pentenenitril to 5-cyanovaleric acid or ester by reacting pentenenitrile with carbon monoxide and water or an alcohol in the presence of a catalyst system, comprising palladium, a bidentate phosphine ligand and an acid having a pKa less than 3, as measured at 18 °C in an aqueous solution,
(b) reduction of 5-cyanovaleric acid or ester as obtained in step (a) to 6-aminocaproic acid or ester,
(c) cyclisation of the 6-aminocaproic acid or ester to ε-caprolactam.

2. Process according claim 1, wherein the bidentate ligand used in step (a) is a compound according to general formula (I):

$$R^1R^2\text{-}P\text{-}R\text{-}P\text{-}R^3R^4 \qquad I$$

wherein R comprises an optionally substituted chain of three or more atoms which directly connect the two phosphorus atoms and R^1-R^4 represent the same or different optionally substituted tertiary alkyl groups.

3. Process as claimed in claim 2, wherein R^1-R^4 represent tertiary butyl groups.

4. Process according to any one of claims 2-3, wherein R is a C_3-C_5 alkylene group.

5. Process as claimed in claim 4, wherein the bidentate ligand is 1,3-bis(di-tert.butylphosphino)propane or 1,2-bis(di-tert.butylphosphinomethyl)benzene.

6. Process according any one of claims 1-5, wherein the temperature in step (a) is between 80 and 120 °C.

7. Process according to any one of claims 1-6, wherein step (b) is performed by contacting the 5-cyanovaleric acid or ester with hydrogen in the presence of a Group VIII metal.

8. Process according to any one of claims 1-7, wherein a mixture of branched and linear carbonylation products as obtained in step (a) is used in steps (b) and (c).

9. Process according to any one of claims 1-8, wherein 5-cyanovaleric acid is obtained in step (a).

10. Process according to any one of claims 1-9, wherein methyl 5-cyanovalerate is obtained in step (a).

11. Process according to any one of claims 1-10, wherein pentenenitrile is obtained by reacting butadiene with hydrogen cyanide.

A B S T R A C T

PROCESS FOR THE PREPARATION OF ε-CAPROLACTAM

Process to prepare ε-caprolactam from pentenenitrile, wherein the following steps are performed:
(a) carbonylation of pentenenitril to 5-cyanovaleric acid or ester by reacting pentenenitrile with carbon monoxide and water or an alcohol in the presence of a catalyst system, comprising palladium, a bidentate phosphine ligand and an acid having a pKa less than 3, as measured at 18 °C in an aqueous solution,
(b) reduction of 5-cyanovaleric acid or ester as obtained in step (a) to 6-aminocaproic acid or ester,
(c) cyclisation of the 6-aminocaproic acid or ester to ε-caprolactam.